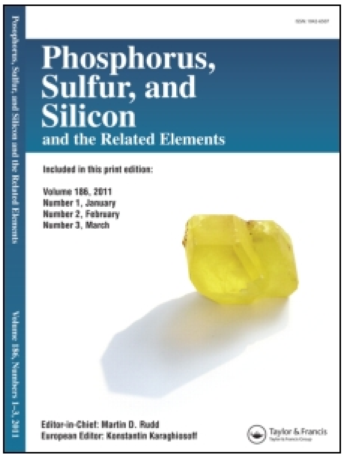

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UPDATING OF PENTACHLOROBENZENESULFONIC ACID

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The sulfonations of pentachlorobenzene (**1**) with 25% oleum at 40°C or 140°C, or with 65% oleum at 40°C give always excellent yields of pentachlorobenzenesulfonic anhydride (**2**). However, pentachlorobenzenesulfonic acid (**3**) is obtained when the working up of the reaction mixture is not mild enough to avoid the hydrolysis of the anhydride **2**. Acid **3** is also synthesized starting from pentachlorophenol (**4**) *via* O-pentachlorophenyl dimethylthiocarbamate (**6**), its isomerization to S-pentachlorophenyl dimethylthiocarbamate (**7**) and final oxidation to **3**. Pentachlorobenzenesulfonyl chloride (**8**) and anhydride (**2**) are also obtained from acid **3**. Anhydride **2** reacts at 200°C with phenol **4** or pentachloroaniline (**10**) giving pentachlorophenyl pentachlorobenzenesulfonate (**9**), or a mixture of pentachlorobenzenesulfonyl pentachloroanilide (**11**) and pentachloroanilinium pentachlorobenzenesulfonate (**12**), respectively. Sulfonamide **11** can be obtained in two polymorphic forms and an ethyl ether solvate, for which interesting spectral and thermal differences are observed.

INTRODUCTION

Within our program on aromatic and alkaromatic chlorocarbons it became of interest to synthesize some derivatives of pentachlorobenzenesulfonic acid (**3**). However, some discrepancies were found in the reported synthetic methods: While Lukashevich[1] in 1954 reported the sulfonation of pentachlorobenzene (**1**) with 65% oleum at room temperature yielding pentachlorobenzenesulfonic anhydride (**2**), m.p. 250–60°C, Cookson[2] in 1972 reported the same sulfonation but yielding pentachlorobenzenesulfonic acid (**3**) dihydrate, m.p. 188–92°C, and Dokunikhin,[3] also in 1972, reported another synthesis of anhydride **2** but with a m.p. 152–3°C. Moreover, Chivers,[4] in 1976, reported the sulfonation of pentachlorobenzene (**1**) with 20% oleum at 165°C yielding acid **3** dihydrate, m.p. 186°C.

RESULTS AND DISCUSSION

In view of the preceding discrepancies, carefully controlled sulfonations of pentachlorobenzene (**1**) were performed, the results being summarized in Table I.

$$\underset{1}{C_6HCl_5} \xrightarrow[\text{or 65 \% oleum}]{\text{25 \% oleum}} \underset{2}{(C_6Cl_5\text{-}SO_2)_2O} \xrightarrow[100°C]{H_2O} \underset{3}{C_6Cl_5\text{-}SO_3H}$$

Table I shows that the sulfonation product depends on the final working up of

TABLE I

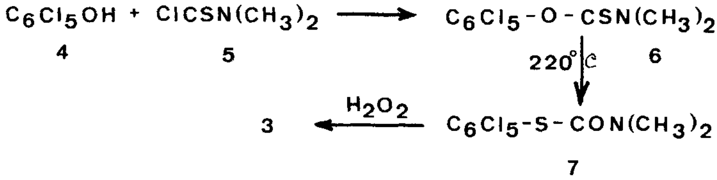
Sulfonations of pentachlorobenzene (**1**)

Oleum conc.	Reaction conditions	Working up method†	Yields Anhyd. **2**	 Acid **3**	 **1** recov.
25%	40°, 30 h.	a	65%	—	30%
25%	140°, 6 h.	a	96%	—	—
25%	140°, 6 h.	b‡	—	90%	—
65%	40°, 24 h.	a	—	95%	—
65%	40°, 24 h.	c	96%	—	—

† See Experimental.
‡ Chivers' method.[4]

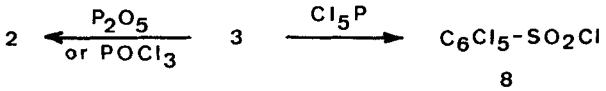
the reaction mixture; when the treatment is mild enough, anhydride **2** is obtained even with 25% oleum at room temperature.

With the purpose of avoiding the use of oleum, a new synthesis of acid **3**, based on the oxidation of S-aryl dimethylthiocarbamates (described by Cooper[5]) was performed. The reaction of pentachlorophenol (**4**) with dimethylthiocarbamoyl chloride (**5**) gives O-pentachlorophenyl dimethylthiocarbamate (**6**)[6], which was isomerized to S-pentachlorophenyl dimethylthiocarbamate (**7**) at 220°C and finally oxidized to acid **3** dihydrate.



$$\underset{4}{C_6Cl_5OH} + \underset{5}{ClCSN(CH_3)_2} \longrightarrow \underset{6}{C_6Cl_5\text{-}O\text{-}CSN(CH_3)_2} \xrightarrow{220^\circ C} \underset{7}{C_6Cl_5\text{-}S\text{-}CON(CH_3)_2} \xrightarrow{H_2O_2} 3$$

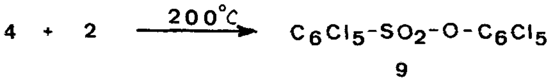
As far as derivatives of acid **3** are concerned, pentachlorobenzenesulfonyl chloride (**8**) is well documented,[1,4,7] its synthesis being confirmed by the authors (see experimental), and the characterization of anhydride **2** was confirmed by anhydrization of acid **3**.



$$2 \xleftarrow[\text{or } POCl_3]{P_2O_5} 3 \xrightarrow{Cl_5P} \underset{8}{C_6Cl_5\text{-}SO_2Cl}$$

Crude anhydride **2** crystallizes with water of hydration, as ascertained by IR spectroscopy, and has vague m.ps.[8] (150–180°C). This water is easily eliminated by solving in benzene and elimination of the solvent by distillation; then the m.p. raises up to 175–85°C (decomp.).

The reaction of dehydrated[9] anhydride **2** with pentachorophenol (**4**) at 200°C gives pentachlorophenyl pentachlorobenzenesulfonate (**9**) along with noticeable amounts of pentachlorobenzene (**1**).



$$4 + 2 \xrightarrow{200^\circ C} \underset{9}{C_6Cl_5\text{-}SO_2\text{-}O\text{-}C_6Cl_5}$$

The presence of **1** (a desulfonation product) is not unexpected since it is already known that sulfonic acids can desulfonate at high temperatures,[10] a reaction that, in this case, is favoured by the presence of two *ortho* chlorines.

While anhydride **2** does not react with pentachloroaniline (**10**) in refluxing benzene, at 200°C they give excellent yields of pentachlorobenzenesulfonyl pentachloroanilide (**11**) and pentachloroanilinium pentachlorobenzenesulfonate (**12**). When anhydride **2** is not dehydrated previously,[9] only an almost quantitative yield of salt **12** is obtained.

$$2 + 2\,\underset{10}{C_6Cl_5\text{-}NH_2} \xrightarrow{200^{\circ}C} \underset{11}{C_6Cl_5\text{-}SO_2\text{-}NH\text{-}C_6Cl_5} + \underset{12}{C_6Cl_5\text{-}SO_3^{-}\cdot \overset{+}{N}H_3\text{-}C_6Cl_5}$$

No desulfonation product is detected here; this is possibly due to the nucleophilicity of the amino group that speeds up the reaction.

The existence of polymorphic forms in sulfonamides is a well known fact.[11] In the present case sulfonamide **11** can be isolated in two polymorphic forms and an ethyl ether solvate, depending on the crystallization procedure (see Experimental). These three forms present appreciable differences in its thermal behaviour (DSC, Differential Scanning Calorimetry) and in the N–H and SO_2 stretching peaks of their infra-red spectra; the data being summarized in Table II.

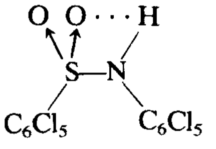
TABLE II

DSC and IR data of polymorphic forms of sulfonamide **11**

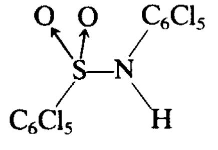
DSC peaks			
α-Form	β-Form	Ether Solvate	CCl_4 Solution
158°C endothermic		~100°C weight loss	
163°C exothermic			
212°C endothermic	212°C endothermic	212°C endothermic	
NH and SO_2 stretching peaks† (in cm^{-1})			
3240	3365	3100–2750	3365
1387 (m)	1387 (s)	1387 (m)	1387 (s)
1368 (s)	1364 (m)	1370 (s)	
1170 (s)	1175 (s)	1176 (s)	1177 (s)

† Normal values:[12] (NH) 3390; (SO_2) 1370–1333 and 1178–1159.

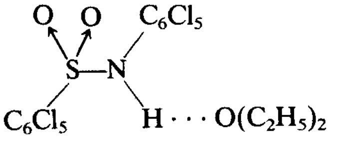
The main IR difference between the α and β forms of sulfonamide **11** is the high frequency shift (125 cm^{-1}) of the N–H stretching band (Figure 1), which in the case of the β form agrees with that obtained in CCl_4 solution. This suggests the presence of a free N–H group in the β form (**11β**) (*trans* conformation), and a bonded N–H group for the α form (**11α**) (*cis* conformation).



(11α)



(11β)



(11s)

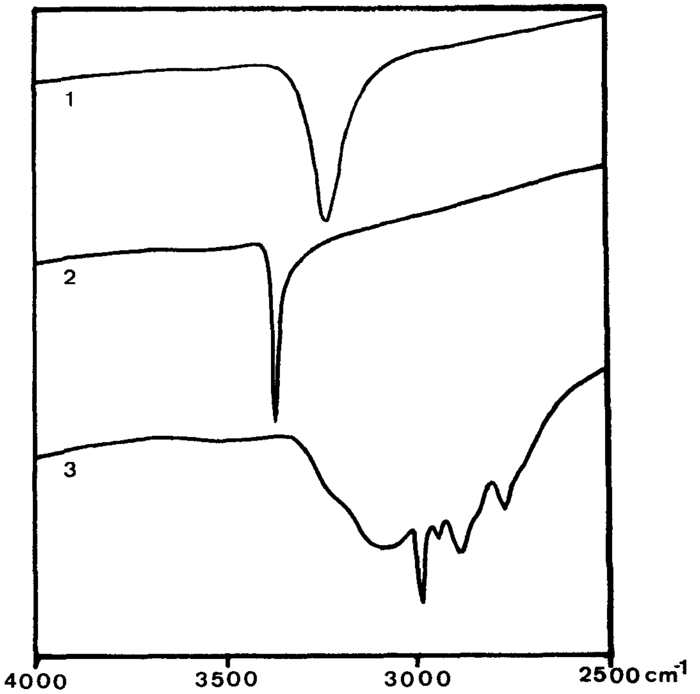


FIGURE 1 N–H stretching band of the IR spectrum of the polymorphs of sulfonamide **11**: (1) α form; (2) β form; (3) solvate.

The great low-frequency shift and broadening of the N–H stretching band in the solvate form of the sulfonamide **11** suggests the formation of an oxonium salt between the highly acidic hydrogen of the NH group and the ethereal oxygen (**11s**). This is in agreement with the fact that ethyl ether is easily eliminated on heating, or under vacuum, affording the β form with the free N–H group. The small frequency shifts observed in the SO_2 stretching bands are also a consequence of the hydrogen bonding between the SO_2 and the N–H groups.

The preceding assignment agrees with the DSC behaviour, since while the β form (with a free N–H) shows only the endothermic peak corresponding to its melting point, the α form (with a bonded N–H) presents a thermogram with three peaks. The two extra peaks around 165°C correspond to the melting point of the α form and its isomerization-re-solidification to the β form that melts at 212°C. In the present case the β form **11β** (with the free N–H) is more stable due to the fact that the two bulky substituents (the pentachlorophenyl groups) are in a *trans* conformation. As far as the ether solvate is concerned, its thermogram shows only a weight loss around 100°C (elimination of ether) and the peak at 212°C corresponding to the melting point of the β form).

EXPERIMENTAL SECTION

Sulfonations of pentachlorobenzene (**1**). *a) With 25% oleum at 40°C (method a).* A mixture of pentachlorobenzene (**1**) (2.030 g) and 25% oleum (20 ml) was heated (40°C; 30 h) with stirring. The resulting mixture was poured slowly into concentrated HCl (200 ml) while cooling (5°C). The precipitate formed was filtered, washed with cool concentrated HCl, dried and extracted with boiling hexane. The organic extract was evaporated to dryness to give starting **1** (0.616 g; 30% recovery). The insoluble residue was dried (in refluxing benzene) and rystallized (same solvent) giving pentachlorobenzenesulfonic anhydride (**2**), (1.602 g; 65%), m.p. 175–85°C (decomp.); IR (KBr) 1520 (w), 1500 (m), 1427 (s), 1418 (s), 1402 (w), 1338 (s), 1315 (s), 1225 (m), 1202 (s), 1175 (m), 1100 (m), 875 (s), 730 (s), 695 (s), 672 (s), 632 (m), 605 (m), 565 (s), 505 (s) cm^{-1}. Anal.: Calcd. for $C_{12}Cl_{10}O_5S_2$: C, 22.4; Cl, 55.1; S, 10.0. Found: C, 22.2; Cl, 55.0; S, 9.9.

b) With 25% oleum at 140°C (method a). A mixture of pentachlorobenzene (**1**) (5.20 g) and 25% oleum (25 ml) was heated (140°C; 6 h) with stirring. The resulting mixture was worked up as in the preceding synthesis to give anhydride **2**, (6.43 g; 96%), identified by m.p. and IR spectrum.

c) With 25% oleum at 140°C (method b). The preceding sulfonation was repeated (pentachlorobenzene (**1**), 5.41 g; 25% oleum, 25 ml; 6 h). The reaction mixture was poured into cracked ice[13] (250 g), concentrated under reduced pressure to about 50 ml and diluted with concentrated HCl (100 ml). The precipitate formed was filtered, washed with concentrated HCl and dried yielding a white solid (6.99 g) showed to be a mixture of anhydride (**2**) and pentachlorobenzenesulfonic acid (**3**) dihydrate (IR spectrum). This solid was solved in boiling water, and the solution concentrated to about 30 ml and diluted with concentrated HCl. The solid formed was filtered and dried to give acid (**3**) dihydrate (7.16 g; 90%), white solid m.p. 186–90°C (Lit., m.p. 188–92°C;[2] 186°[4]), identified by m.p., acid equiv., IR spectrum, and elemental analyses.

d) With 65% oleum at 40°C (method a). A mixture of pentachlorobenzene (**1**) (2.180 g) and 65% oleum (20 ml) was stirred (24 h) at 40°C. The resulting mixture was worked up as in paragraph a) to give acid **3** dihydrate (3.015 g; 95%) identified as before.

e) With 65% oleum at 40°C (method c). The preceding sulfonation was repeated (pentachlorobenzene (**1**), 2.040 g; 65% oleum, 10 ml; 24 h). The resulting mixture was poured slowly over cool (0–5°C) concentrated H_2SO_4 and then over cool (0–5°C) concentrated HCl (500 ml). The precipitate formed was filtered, washed with cool concentrated HCl and dried to give hydrated anhydride **2** (2.685 g) which was dried over refluxing benzene and crystallized (same solvent) to give anhyride **2** (2.512 g; 96%), identified as before.

O-Pentachlorophenyl dimethylthiocarbamate **6**. A mixture of pentachlorophenol (**4**) (0.267 g), KOH (0.25 g), dimethylcarbamoyl chloride (**5**) (0.130 g) and dioxane (10 ml) was stirred for 1 h at 30°C and 3 h at 85°C. The reaction mixture was diluted with water (15 ml) and extracted with $CHCl_3$. The organic layer was washed with aqueous 2N HCl and with water, dried and evaporated. The residue, by crystallization ($CHCl_3$-pentane) gave thiocarbamate **6** (0.340 g; 96%) as white needles; DSC, 183°C (endothermic, m.p.), 224°C (exothermic, isomerization) (Lit.;[6] m.p. 182.5–3.5); IR (KBr) 2920 (w), 1530 (s), 1380 (s), 1358 (s), 1274 (s), 1247 (s), 1165 (s), 1088 (s), 778 (s), 730 (m), 705 (m) cm^{-1}; ^1H NMR: 7.30 (s, 3H), 7.50 (s, 3H). Anal.: Calcd. for $C_9H_6Cl_5NOS$: C, 30.6; H, 1.7; N, 4.0. Found: C, 31.0; H, 1.7; N, 4.1.

S-Pentachlorophenyl dimethylthiocarbamate (**7**). O-Thiocarbamate **6** (0.100 g) was heated at 220°C (25 min) and recrystallized ($CHCl_3$-pentane) to give S-thiocarbamate **7** (0.088 g; 88%), m.p. 141–3°C; IR (KBr) 2900 (w), 1660 (s), 1360 (s), 1330 (s), 1305 (s), 1245 (m), 1080 (s), 900 (m), 870 (m), 682 (s), 662 (s) cm^{-1}; ^1H NMR: 7.10 (s, 6H). Anal.: Calcd. for $C_9H_6Cl_5NOS$: C, 30.6; H, 1.7; N, 4.0; S, 9.1. Found: C, 30.5; H, 1.7; N, 3.9; S, 9.1.

Pentachlorobenzenesulfonic acid (**3**). A mixture of 98% formic acid (0.8 ml) and 30% H_2O_2 (0.3 ml) was added to a solution of S-thiocarbamate **7** (0.066 g) in $CHCl_3$ (1.5 ml). The resulting solution was stirred for 18 h at room temperature, poured into water, decanted, and the organic layer washed with water. The aqueous phases were evaporated to dryness in vacuo to give acid **3** dihydrate (0.030 g; 49%), identified as before.

Pentachlorobenzenesulfonyl chloride (**8**). A mixture of sulfonic acid **3** (7.00 g), Cl_5P (33.4 g) and benzene (130 ml) was refluxed (36 h) with stirring. The resulting mixture was poured into cracked ice and extracted with benzene. The organic layer was washed with water, dried and evaporated. The residue was purified through silicagel ($CHCl_3$) yielding acid chloride **8** (5.770 g; 86%), m.p. 74–5°C, which was identified by m.p. (Lit.:[4] 76–7°C) and IR spectrum. IR (KBr) 1515 (m), 1490 (s), 1400 (s), 1380 (s), 1335 (s), 1320 (s), 1310 (s), 1220 (s), 1205 (m), 1190 (s), 1100 (s), 875 (s), 720 (m), 705 (m), 670 (s), 635 (m), 615 (s), 540 (s) cm^{-1}

Pentachlorobenzenesulfonic anhydride (**2**). *a*) *With $POCl_3$.* A mixture of sulfonic acid **3** (0.510 g) and $POCl_3$ was refluxed (2 h) with stirring. The resulting mixture was poured into cracked ice and the precipitate formed was filtered, washed with cool water and dried. The resulting solid was recrystallized from cool $CHCl_3$ (−40°C) yielding anhydride **2** (0.102 g), identified as before.

b) *With P_2O_5.* A mixture of sulfonic acid **3** (0.243 g), P_2O_5 (0.735 g) and $CHCl_3$ (50 ml) was stirred (30 min) at room temperature, filtered and the solid extracted with refluxing $CHCl_3$ (Soxhlet, 30 min), the organic layer was evaporated and recrystallized as before to give anhydride **2** (0.161 g; 76%), identified as before.

Pentachlorophenyl pentachlorobenzenesulfonate (**9**). A mixture of anhydride **2** (1.000 g) and pentachlorophenol (**4**) (0.402 g) was solved in refluxing benzene (100 ml), the solvent was distilled off, and the resulting mixture was heated at 200–10°C (30 min) in a sealed glass tube. The dark residue was extracted with boiling $CHCl_3$ leaving insoluble acid **3** dihydrate (0.564 g; 99%). The organic extract was evaporated to dryness and chromatographed over silicagel to give pentachlorobenzene (**1**) (hexane) 0.125 g; 32%) and a solid (CCl_4) which was submitted to sublimation (100°C, 0.01 mm) yielding pentachlorophenol (**4**) (0.173 g; 43% recovery) and a residue of sulfonate **9** (0.345 g; 39%), m.p. 199–202°C; IR (KBr) 1620 (w), 1598 (m), 1428 (s), 1416 (s), 1376 (s), 1362 (s), 1312 (s), 1220 (m), 1195 (s), 1173 (m), 970 (s), 875 (s), 794 (s), 742 (m), 710 (s), 690 (s), 635 (m), 566 (s), 535 (m), 508 (s) cm^{-1}. Anal.: Calcd. for $C_{12}Cl_{10}O_3S$: C, 24.9; Cl, 61.3; S, 5.5. Found: C, 25.2; Cl, 61.2; S, 5.3.

Pentachlorobenzenesulfonyl Pentachloroanilide (**11**). A mixture of anhydride **2** (0.648 g) and pentachloroaniline (**10**) (0.538 g) was dehyrated with benzene as in the synthesis of sulfonate **9**, then heated at 200°C (15 min) and extracted with refluxing $CHCl_3$. The insoluble residue was solved in dioxane, passed through silicagel, evaporated to dryness and digested with boiling $CHCl_3$, yielding pentachloroanilinium pentachlorobenzenesulfonate (**12**) (0.547 g; 91%), m.p. dec. 290°C. IR (KBr) 3500–2500 (m), 1570 (w), 1540 (w), 1515 (m), 1384 (s), 1370 (s), 1335 (s), 1310 (s), 1220 (s), 1150 (s), 1110 (s), 1043 (s), 960 (m), 867 (m), 680 (s), 600 (s), 472 (m) cm^{-1}. Anal.: Calcd. for $C_{12}H_3Cl_{10}NO_3S$: C, 24.2; H, 0.5; Cl, 59.5; N, 2.4; S, 5.4. Found: C, 24.3; H, 0.5; Cl, 59.1; N, 2.5; S, 5.6.

The $CHCl_3$ solution was purified through silicagel and evaporated. The residue was recrystallized (CCl_4 or $CHCl_3$) affording sulfonamide **11** (α isomer) (0.429 g; 74%); DSC: 165°C (endothermic), 169°C (exothermic), 212°C (endothermic); IR (KBr) 3240 (m), 1515 (w), 1500 (w), 1418 (s), 1387 (m), 1368 (s), 1340 (s), 1310 (s), 1170 (s), 1100 (m), 990 (m), 890 (m), 790 (m), 695 (m), 674 (m), 642 (m), 564 (s), 508 (m) cm^{-1}. Anal.: Calcd. for $C_{12}HCl_{10}NO_2S$: C, 24.9; H, 0.2; Cl, 61.4; N, 2.4; S, 5.6. Found: C, 25.1; H, 0.2; Cl, 61.5; N, 2.5; S, 5.4.

The heating of sulfonamide **11** (α isomer) at 175°C (10 min) or recrystallization from refluxing hexane yields sulfonamide **11** (β isomer); DSC: 212°C (endothermic); IR (KBr) 3365 (m), 1500 (w), 1418 (s), 1387 (s), 1364 (m), 1331 (s), 1308 (s), 1175 (s), 1095 (m), 982 (m), 880 (s), 790 (m), 695 (m), 671 (m), 640 (m), 564 (s), 508 (m) cm^{-1}. Anal.: Calcd. for $C_{12}HCl_{10}NO_2S$: C, 24.9; H, 0.2; N, 2.4; S, 5.6. Found: C, 25.2; H, 0.2; N, 2.3; S, 5.4. Recrystallization of sulfonamide **11** (β isomer) in CCl_4 or $CHCl_3$ gives back the α isomer.

Recrystallization of both α and β isomers of sulfonamide **11** in ethyl ether gives an ether adduct with IR (KBr) 3100 − 2750 (m), 1515 (w), 1500 (w), 1418 (s), 1387 (m), 1370 (s), 1344 (s), 1331 (s), 1308 (s), 1176 (s), 992 (m), 883 (s), 790 (m), 692 (s), 670 (m), 638 (m), 563 (s), 508 (m) cm^{-1}. Heating of this adduct at 100°C, or under vacuum it yields sulfonamide **11** (β isomer). The TG curve of the solvate shows a weight loss corresponding to 0.91 moles of ethyl ether.

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13. Care must be taken in order to use distilled water, since when the ice is obtained from normal tape (non deionized) water, variable amounts of sodium pentachlorobenzenesulfonate[2] are obtained along with the acid **3** dihydrate.